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Reid E. Basher

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Total Ozone Measurement: Intercomparison of Prototype New Zealand Filter Instrument and Dobson Spectrophotometer

Reid E. Basher
Wallops Flight Center
Wallops Island, Virginia

National Aeronautics
and Space Administration

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TOTAL OZONE MEASUREMENT: INTERCOMPARISON OF PROTOTYPE NEW ZEALAND FILTER INSTRUMENT AND DOBSON SPECTROPHOTOMETER

by

Reid E. Basher
Wallops Flight Center

SUMMARY

An intercomparison of a prototype New Zealand narrowband interference filter instrument with a Dobson prism instrument was made at Wallops Island (37°51'N, 75°29'W) from December 1976 to May 1977. About 400 Dobson and 4000 filter instrument total ozone measurements were taken. A linear regression for airmasses less than two and an ozone range of 0.300 to 0.500 atm cm shows the relationship:

$$X_{AD}(\text{filter}) = 0.9303\ X_{AD}(\text{Dobson}) - 0.0014, \text{ std. dev.} = 0.0061 \text{ atm cm}$$

i.e., this filter instrument differs from the Wallops Island Dobson instrument by a multiplicative bias of (-7 ± 1.7)%. The 1.7% standard deviation and -0.0014 intercept indicate a very good proportionality between the two instruments. The -7% bias is smaller than the intercomparison uncertainty of 9 to 13% from calibration sources. The relationship shows an airmass dependence, owing to a fall off in Dobson instrument values near an airmass of 2.8, but the filter instrument values are generally constant to 2% at an airmass of 4.0. A residual 1% drift in the relationship during the first hour of measurements was found to be due to the filter instrument's slowness in reaching its thermostatic equilibrium. Long term drift in the relationship was negligible, however, at about 0.05% per month. Further effort to reduce calibration uncertainties will be needed to improve the intercomparability of the two instruments in future.

INTRODUCTION

The Dobson double prism spectrophotometer is the acknowledged standard instrument for measuring atmospheric total ozone, and certainly it is the most widespread and often used instrument. However, it suffers from some disadvantages, namely, it is manually operated, requires skillful operation, maintenance and calibration, and is relatively large, heavy and not portable (References 1, 2, 3, 4, and 5). In consequence, alternative instruments have been developed, among them being the New Zealand filter instrument, the principal subject of this note.

The filter instrument was developed at the University of Canterbury in New Zealand as a filter wheel photometer exploiting the development of narrowband ultraviolet interference filters. It met reasonable criteria of simplicity, portability, automation and ease of operation, and had a good spectral band purity, comparable with that of the Dobson instrument, and far exceeding that of the absorption-glass type of filter instrument (References 6, 7 and 8). There remained, however, a number of questions concerning its accuracy, long term stability and comparability to the Dobson instrument, questions which could be answered in part by a long-term field test and direct intercomparison with a Dobson instrument. Previous intercomparisons of early prototypes had been rather short and inconclusive (Reference 6).

Informal contact between staff of the University of Canterbury and NASA Wallops Flight Center eventually led to a formal agreement that the Center evaluate an instrument loaned by the University, and this in turn evolved into an intercomparison. The project was undertaken by the author, who formerly had helped in the instrument's development at the University. The loaned instrument was a prototype whose filters, though tilted, could not be tuned in the manner described in Reference 7 to approximate the Dobson slit band wavelengths. Some caution, therefore, is needed in applying the results of this study to later commercial models of the instrument.

Briefly then, the aims of the work reported here were to intercompare the filter instrument with a Dobson instrument over a lengthy period, to detect any systematic errors in the filter instrument, and to assess the practical problems of its field operation.

FIELD INTERCOMPARISON

The data described in this section consist entirely of direct-sun mode X_{AD} total ozone measurements. (For definitions of these terms and the basic theory of total ozone measurement, see References 1 and 9.) They were taken at Wallops Island (latitude 37° 51' N, longitude 75° 29' W) during the five-month winter and spring period between December 22, 1976 and May 27, 1977, and cover a range of 0.300 to 0.500 atm cm in Dobson total

ozone, a range of 1.0 to over 4.0 in airmass, and a range in ambient temperature of -3° to +18°C. Almost all of the filter instrument measurements and about 85% of the Dobson measurements used were made by an observer who was initially inexperienced with both instruments. There were no systematic differences between these Dobson measurements and the remaining 15% which were made by regular NOAA observers. About 400 Dobson and 4000 filter instrument measurements were made altogether, and a set of 400 filter values was constructed from means of the six measurements closest to, and within thirty minutes of, the Dobson values.

The instruments were calibrated independently. The Dobson instrument's calibration was checked in April 1976 by Mr. R. D. Grass of NOAA's Geophysical Monitoring for Climatic Change group which has charge of the United States Dobson network, and routine monthly tests were continued by local NOAA personnel. A description of the filter instrument's calibration is given later under calibration as the topic is of sufficient importance to merit a separate section.

A plot of daily ozone amounts for the available days, figure 1, shows that the instruments track well together over the ozone variation, but with a bias, the filter

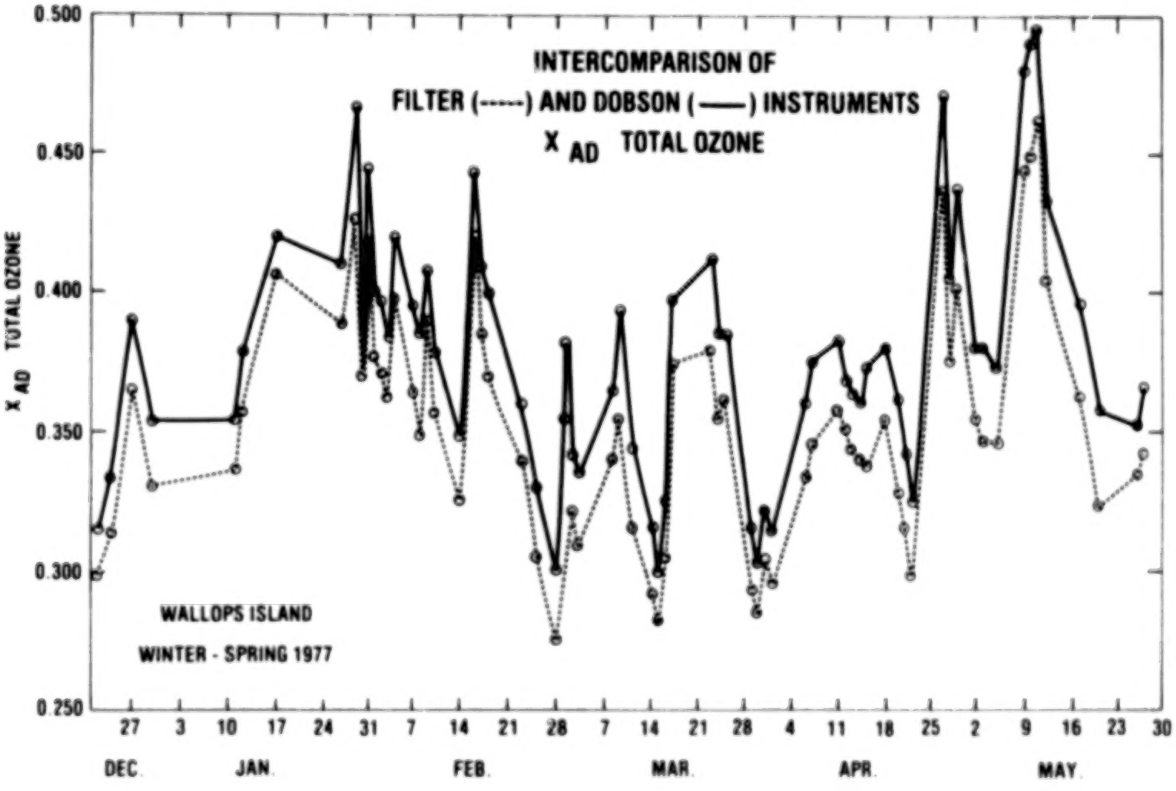
INTERCOMPARISON OF
FILTER (-----) AND DOBSON (——) INSTRUMENTS
X AD TOTAL OZONE
X AD TOTAL OZONE
0.500
0.450
0.400
0.350
0.300
0.250
WALLOPS ISLAND
WINTER - SPRING 1977
27 3 10 17 24 31 7 14 21 28 7 14 21 28 4 11 18 25 2 9 16 23 30
DEC. JAN. FEB. MAR. APR. MAY.

Figure 1. The New Zealand filter instrument and the Dobson prism instrument X_{AD} ozone values track well together, but with a bias of (7 ± 1.7%). The bias is within the intercomparison calibration uncertainty.

instrument reading lower than the Dobson instrument. A linear regression, for airmasses less than two, confirms this with the following relationship,

$$X_{AD}(\text{filter}) = 0.9303\ X_{AD}(\text{Dobson}) - 0.0014, \text{ std. dev.} = 0.0061, \text{ atm cm.} \qquad (1)$$

The 0.0014 additive bias is negligibly small, and along with the small standard deviation, indicates a very good proportionality between the two instruments. Since the mean Dobson X_{AD} was 0.370 atm cm, the remainder of the equation can be summarized as a $(-7.0 \pm 1.7)\%$ multiplicative bias. However, the 7% figure is within the 9% to 13% uncertainty in the intercomparison due to calibration sources (see Calibration section), and therefore it does not necessarily represent a real bias or an unresolved error in either instrument. A smaller bias would be desirable of course, but it is clear that a substantial effort to reduce the calibration uncertainties of both instruments would be needed to improve upon the present result, and even then the practical limit of the uncertainty may be about 4%. The 0.0061 atm cm or 1.7% standard deviation is important as it indicates the constancy of the bias, and it compares well with the 0.005 value found for a grating instrument-to-Dobson intercomparison and the 0.002 to 0.008 values for Dobson-to-Dobson intercomparisons (Reference 10).

The data described above are restricted to airmasses less than 2 owing to an airmass dependence in the bias relationship. The dependence, which is illustrated in figure 2, is largely due to a decline in the Dobson X_{AD} values that becomes noticeable at an airmass of

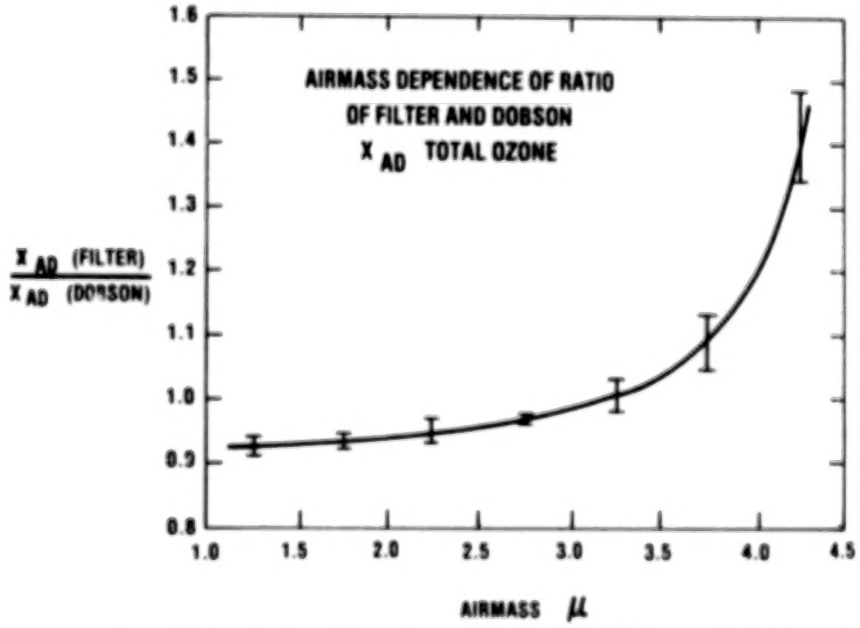

Figure 2. The relationship of the filter instrument and Dobson instrument X_{AD} ozone amounts is airmass independent, owing to the well-known airmass dependence of the Dobson instrument.

about 2.8. This is a well known Dobson behavior and is usually avoided by simply not taking measurements of the offending A wavelength pair beyond some suitably established airmass, substituting instead the C wavelength pair, or by using the "focussed image" technique (References 1, 2, 3 and 4). The accelerating increase in the bias relationship with airmass rules out error in extraterrestrial constants as a major source of the dependence. The data showed that the filter instrument's X_{AD} airmass dependence is typically less than 2% at an airmass of four.

To check for any long-term drift in the 7% bias relationship, the ratio X_{AD}(filter)/ X_{AD}(Dobson) was regressed linearly against time. The first result, for the airmass interval 1.0 to 2.0, was -0.29% per month, but this value can be fully accounted for by the bias relationship's airmass dependence coupled with the seasonal shift in midday airmass values. This was confirmed by the following calculations for finer divisions of airmass. The results for the airmass intervals between 1.0, 1.5, 2.0, 2.5 and 3.0 were respectively +0.08, +0.02, +0.02 and -0.04% per month, and are probably near to the limits of detectability. In other words, there is little evidence of long-term drift in the relationship between the filter and Dobson instruments. The detection and correction of any long-term drift in the filter instrument should in future be carried out by comparing the instrument with spectral and standard lamps, rather than by the more uncertain and difficult method of comparing it in the field with a Dobson instrument.

There was a difficulty with the filter instrument's thermostatic system which is not readily apparent in the above results. The problem is the unexpectedly long time required to establish the filters' thermostatic equilibrium and the consequent systematic errors in the X_C and X_D ozone amounts during the first hour after the instrument is turned on. During the intercomparison the instrument was turned on about thirty minutes before measurements were made, but there still remained a residual temperature effect which appeared to amount to a 1% drift in the X_{AD} total ozone. The next section discusses the point in more detail.

Some comments about the practical operation of the filter instrument bear mentioning. The performance of the equatorial mount was not fully satisfactory. The mount was poorly balanced, the fine adjustments for the photometer's alignment on the sun were difficult to manage, and sometimes alignment was lost in gusty wind conditions. The thermostatic device to control the interference filters' temperatures also showed deficiencies. Occasionally at high ambient temperatures the internal temperature was driven up out of control, while at low ambient temperatures very long warming periods were required, sometimes with the design temperature of 40°C never being reached.

On the positive side, the filter instrument, being semi-automatic, produced much more data than the Dobson instrument, and did so with relatively little effort on the part of the operator. The operator noted with appreciation the ease of reading the digital data

output display, and more importantly, the absence of any required judgment skill, such as is needed in choosing null positions and setting lever positions on the Dobson instrument.

TEMPERATURE EFFECTS

In preliminary testing before the intercomparison began it was found that the X_D and to a lesser extent X_C ozone amounts exhibited unusually large systematic changes over the first half hour of operation, usually in the form of an approximately exponential decay and therefore suggesting a cause dependent on the rising temperature of the instrument's thermostatic filter chamber. A simple center wavelength shift of the interference filters (Reference 7) was insufficient to account for the size of the changes and since at that point it was realized that the transmittance of the instrument's nickel sulphate blocking filter was temperature dependent, the blame was attached to it.

During the intercomparison itself the problem was countered by including the blocking filter within the thermostatic chamber and by allowing an instrument warm up period of at least thirty minutes. These precautions did avoid the worst of the problem, but there still remained a noticeable effect, and so at the end of the intercomparison the instrument was withdrawn into the laboratory for further investigation. The basic test involved running the instrument from cold, on a well-stabilized tungsten halogen lamp, and taking measurements every subsequent minute or half minute for about ninety minutes, or until a temperature equilibrium had been established. Ratios of the measured intensities for the various bandpairs were then compared with an average ratio derived from the last ten equilibrium measurements. If no temperature dependence existed, the ratios would have remained constant for the whole experiment. The aim of the tests was to isolate the components contributing to the temperature effect.

The results can be summarized as follows:

(1) For an unaltered cold (20°C) instrument the errors in the decimal logarithm of the intensity ratios (equivalent to an extraterrestrial constant error) were initially --0.008, -0.014 and -0.032, respectively, for the A, C, and D wavelength pairs, and typically declined to one tenth of these values within thirty minutes. The errors were repeatable, i.e., the effect is reversible, but when divided by the wavelength difference of the band pair, showed little evidence of a smooth wavelength variation.

(2) Removal of the nickel sulphate blocking filter changed the initial log ratio errors by up to 0.010, but did not result in any major overall reduction of error. This was confirmed by the introduction of a cold blocking filter into an otherwise equilibrated instrument, and by a similar introduction of the interference filter wheel.

(3) The photomultiplier, whose end forms one window of the thermostatic chamber, appeared to contribute less than 0.003 to the initial log ratio errors.

It is clear from the above that the interference filters have sizeable temperature dependences and are slow to rise to the intended thermostatic equilibrium temperature. The size of the resulting errors, equivalent to relative flux changes of up to 7%, together with the lack of smoothness in the wavelength variation of the effect, points to changes in peak transmittance and bandwidth of the double filter combinations which comprise each band, i.e., to relative spectral sensitivity changes, rather than to any simple shift in center wavelength relative to the lamp spectrum. The origin of such changes is unknown at present, but it may be due to the temperature gradients across the filters or to changes in the relative orientation of the two tilted filters that make up each band.

At present the filter instrument needs to be turned on one hour before measurements are taken. It seems likely that the filters themselves will always require a similar period to reach equilibrium since they are poor conductors and the transfer of heat to them by convection is a slow process. However, it would be quite feasible in future to maintain them at elevated equilibrium temperatures continuously, thus avoiding warm up times altogether. The filters can be operated at up to 60°C, and the method would have the important advantage of significantly reducing the harmful mechanical stressing that accompanies their warming and cooling.

CALIBRATION

Filter instrument calibration involves two things, first, the filter bands' ozone absorption coefficients must be calculated, and second, for the chosen pairs of bands, the extraterrestrial constants must be determined (the constant is the logarithm of the ratio of the bands' responses in the hypothetical absence of the atmosphere).

To find the ozone absorption coefficients, the filters' spectral transmittances were measured with a Cary 14 Recording Spectrophotometer and were approximated by a symmetrical nine-coefficient polynomial model filter, suitably scaled by center wavelength and bandwidth. The filter models, which extend to 4×10^{-5} times the peak transmittances and to six times the half bandwidths, were integrated over a 0.1 nm ozone absorption spectrum and atmospheric model to give the filters' ozone absorption coefficients as a function of airmass and total ozone. (The calculation method is described in Reference 8.) At the same time Rayleigh scattering coefficients and 'initial guess' extraterrestrial constants were calculated.

To check the computer program used, the ozone absorption coefficients for two widths of Dobson slits were also calculated. The A, C and D wavelength pair coefficients, scaled by the convention that makes the AD coefficient equal to 1.388, are listed in Table 1, along with the scaling factors, the current standard IOC 1968 coefficients (Reference 11), and a set of coefficients determined experimentally with a Dobson instrument (References

TABLE 1. DOBSON OZONE ABSORPTION COEFFICIENTS
in (atm cm)

Wavelength Combination	A	C	D	AD	AD Scaling Factor
0.9, 2.9 nm Slitwidth	1.750	0.814	0.362	1.388	0.9976
1.0, 3.0 nm Slitwidth	1.744	0.805	0.356	1.388	0.9912
1968 IOC Std. Values	1.748	0.800	0.360	1.388	--
Dobson Lab. Experiment	1.744	0.809	0.356	1.388	--

12 and 13). The agreement is very satisfactory. The filter instrument's ozone absorption coefficients were found to be 1.7766, 0.7244, 0.3579 and 1.4187 for the A, C, D and AD wavelength combinations respectively, and are quite different from the Dobson coefficients because the filter bands of this prototype are up to 1.0 nm away from the corresponding Dobson bands.

The coefficients' uncertainty is largely controlled by the 0.2 nm wavelength uncertainty which is inherent in Cary 14 calibrations of interference filters (Reference 7). This amounts to 2% for the AD coefficient. Additional uncertainty, relative to the Dobson coefficients, arises from the above-mentioned differences in center wavelengths between the filter and Dobson bands, and the inaccuracies of the ozone absorption data used to calculate the coefficients. The problem is that the Vigroux 1967 revised data (Reference 14), from which the current Dobson coefficients are calculated, do not extend beyond the immediate spectral regions of the Dobson bands, and that therefore the parts of the filter bands lying outside these regions must rely on the more comprehensive but less consistent Vigroux 1953 data (Reference 15). The 1967 revision resulted in changes in the Dobson A, C, D and AD coefficients of -0.9%, -6.7%, -2.4% and -0.5%, respectively. Therefore a reasonable assessment of the uncertainty in the relative accuracy of the filter instrument and Dobson AD coefficients due to this cause is 1%, but the figure for the C pair coefficient could be somewhat higher.

The uncertainty in the intercomparison due to the calibration of the Dobson instrument must also be considered. Calculations of the Dobson ozone absorption coefficients show that uncertainties of ±.05 nm in both slitwidth and slit position result in a 1% uncertainty in the AD coefficient, and to this must be added an uncertainty of at least 1% due to uncertainty in the optical wedge calibration and in the derivation and application of the temperature correction. Combining the uncertainties from both filter and Dobson instruments gives a total intercomparison uncertainty, due to AD ozone absorption coefficient calibration, of 5%.

As already noted, a by-product of the calculation of the ozone absorption coefficients is the calculation of extraterrestrial constants. Unfortunately, the values

obtained are not sufficiently accurate for calibrating the filter instrument and so conventional experimental determinations must be resorted to. The calculated values are, however, useful as "initial guess" starting points in these determinations. In the experimental method used, a half-day's ozone values were calculated using the initial guess extraterrestrial constants and were plotted against 1/airmass. It can be shown that the error in the initial guess constant is equal to the slope of this graph times the appropriate ozone absorption coefficient, provided the atmosphere's relative spectral attenuation and the instrument's relative spectral sensitivity were constant during the course of the measurements. Notice that for best accuracy, the range of 1/airmass should be as large as possible.

Sixteen half-days of intercomparison measurements were chosen for the determination. There were equal numbers of mornings and afternoons in the sample, and each half-day's result was weighted by factors 1, 2 or 3 according to an empirical assessment of the quality of the half-day's original measurements. For illustrative purposes, Table 2 lists the errors found in the initial guess extraterrestrial constants. Below each is listed a

TABLE 2. EXTRATERRESTRIAL CONSTANT DETERMINATION

Wavelength Combination	A	C	D	AC	AD	CD	Dobson AD
Error in Initial Guess	0.037	0.021	-0.083	0.016	0.125	0.107	0.005
± Standard Deviation	0.037	0.038	0.053	0.045	0.082	0.032	0.049
Max. Expected Error	0.162	0.078	0.049	0.076	0.114	0.029	0.111

more important number, the standard deviation of the determination, which reflects any lack of constancy in atmospheric relative spectral attenuation and instrument relative spectral sensitivity during the measurements. The former can be assessed as follows.

The error in extraterrestrial constant determined from a half-day's data due to the maximum expected change in aerosol character is about 0.020 for the A, C and D single wavelength pairs and near zero for the double wavelength-pairs, while that due to a maximum expected ozone change of 10% per half-day is about 0.080 times the appropriate ozone absorption coefficient. The totals of these maximum expected errors are also listed in Table 2. Comparison of the standard deviations with the maximum expected errors shows that while the A pair's standard deviation is well below the maximum expected, most of the other pairs have values similar to the maximum expected. This in turn suggests that the filter instrument lacks sufficient constancy in the relative spectral sensitivity of its longer wavelength bandpairs. The graphical data indicates that the residual temperature dependence described under Temperature Effects is a probable cause. However, to be weighed against this evidence is the 1.7% standard deviation in the ratio of filter

instrument to Dobson instrument AD total ozone derived from the intercomparison and described earlier. This value requires an actual constancy for the AD combination that is about six times better than the ±0.082 value given in Table 2. Further effort should be made to resolve this question, since constancy in relative spectral attenuation is an important instrumental requirement.

Data for the Dobson AD bandpair combination are also listed in Table 2. The small error determined for the extraterrestrial constant shows that the sixteen half-day sample had a small average change in atmospheric relative spectral attenuation (assuming that the Dobson instrument's constants are accurate) and therefore that the sample is a suitable one for calibrating the filter instrument. The Dobson AD standard deviation is smaller than the filter AD standard deviation but is still rather large. This probably is due to real ozone changes and to the airmass dependence described under Field Comparison.

Comparison of the Dobson and filter instrument cases suggests a real uncertainty (as distinct from uncertainty due to ozone change) of 0.040 in the instruments' relative AD extraterrestrial constant. This is equivalent to 0.030/airmass or about 8%/airmass in total ozone. Altogether then, the total uncertainty in the intercomparison of the AD total ozone amounts from the two instruments is about 5% + 0.030/airmass.

Three concluding points can be made. First, it should be noted that the filter instrument's calibration is independent of the Dobson instrument's calibration. This approach is to be distinguished from the regression method, used in the preliminary intercomparison of the grating instrument with a Dobson instrument (Reference 10), which forces a mean bias of zero between the intercompared instruments. Second, though the winter-spring period is the most interesting period for an intercomparison, because the ozone is high and highly variable, for the same reason it is the poorest for determining extraterrestrial constants. Ideally, the constants should be determined during the summer or autumn and their uncertainties reduced to the 0.005 level, but a practical alternative, being developed for the global network of Dobson instruments, is to determine the constants of one reference instrument exceptionally well, and to transfer these determinations to other instruments by direct intercomparison. Third, the filters of the prototype filter instrument used in this project could not be tuned to approximate the Dobson wavelengths and were not calibrated through use of the "discriminator filter" method (Reference 7). The application of these techniques to future filter instruments will improve their intercomparability with Dobson instruments.

CONCLUSION

The intercomparison's 400 point sample of field data, gathered over five months of very variable ozone, showed that on average the prototype filter instrument gave AD total

ozone values that were 0.93 times the Dobson instrument's. The standard deviation of the relationship was 1.7%, indicating a good proportionality between the instruments, and the 7% bias was less than the 9% to 13% intercomparison uncertainty (the bulk of which arose from the filter instrument's calibration). The relationship showed negligible long-term drift, but it was found to be dependent on airmass, owing to a relatively large airmass dependence in the Dobson instrument. Compared to the Dobson instrument, the filter instrument was simple to operate, though a number of mechanical, electronic and optical inadequancies were noted during the field work.

The most serious problem found was an unexpectedly large variation in the filter instrument's relative spectral sensitivity as the thermostatic chamber warms up. A laboratory study showed that the interference filters cause most of the variation, though the effect is much greater than that due to temperature shift in center wavelength alone. The disadvantage of the variation is the inconvenience of the long, one hour, warm up periods needed, but this could be circumvented in future by maintaining the equilibrium temperature continuously.

The filter instrument was calibrated by integrating measured filter spectra over an ozone absorption spectrum to give absorption coefficients, and by determining extra-terrestrial constants from field measurements. Extraterrestrial constant determination is a difficult task for any UV total ozone instrument, and in this study the difficulty was worsened by high and highly variable ozone amounts and by the instrument's residual temperature dependence. The Dobson instrument was calibrated independently by the NOAA personnel in charge of it.

The intercomparison's main value was in providing the large set of filter instrument versus Dobson instrument total ozone data from which the simple ($-7.0 \pm 1.7\%$) bias relationship can be derived, and in pointing up a number of deficiencies in the filter instrument. To be useful, any further intercomparison will need to make a significant advance upon this situation in order to justify the effort involved, and therefore will require very careful planning, preparation and execution. In particular, prior to any field work, there should be good evidence presented to show that the filter instrument to be used has its temperature problems eliminated and can be calibrated by well-tested, routine methods, that the Dobson instrument to be used has the least possible airmass dependence, and that both instruments are especially well calibrated.

Until such a point is reached, all efforts should be concentrated on solving the problems raised by this intercomparison. Though at present the filter instrument cannot be considered as a fully independent total ozone monitor, it can be used with confidence if a bias relationship is established by a comparison to a reputable Dobson instrument. This "calibration by comparison" method is essentially the same as that currently being established within the global Dobson instrument network.

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*NRC-NASA Resident Research Associate

16. Abstract

A five month intercomparison at Wallops Island showed that the X_{AD} total ozone amounts of a prototype New Zealand narrowband interference filter instrument were 7% (± 1.7% std. dev.) less than those of a Dobson instrument for an ozone range of 0.300 to 0.500 atm cm and for airmasses less than two. The 7% bias was within the intercomparison calibration uncertainty. An airmass dependence in the Dobson instrument made the bias relationship airmass-dependent but the filter instrument's ozone values were generally constant to 2% up to an airmass of four. Long-term drift in the bias was negligible. Calibration uncertainties will need reducing to improve the instruments' intercomparability in the future.

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